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Polynitrogen Chemistry: Recent Development in Pentazole and Polyazide Chemistry



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Why Polynitrogen Compounds ?



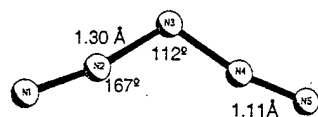
- Polynitrogen compounds contain only nitrogen atoms and are expected to have unusual properties. Most important among these are:
 - *High endothermicity*
 - *"Green" propellant*
"combustion" product is only gaseous N₂
 - *High density*
 - *High I_{sp} values when compared to other monopropellants or bipropellants*
 -  *High detonation velocity*



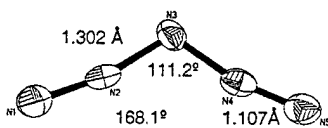
Geometry of the N_5^+ cation



V-Shaped Geometry

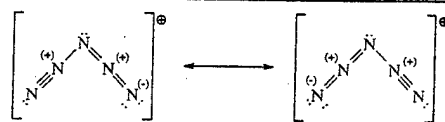


Calculated Structure

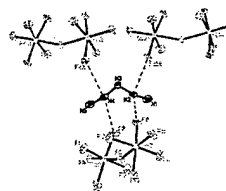


Experimental Structure

Vij, Wilson, Vij, Tham, Sheehy & Christie,
J. Am. Chem. Soc., 2001, 123, 6308-6313



Resonance Structure



N2 makes contacts at 2.723 and 2.768 Å
N4 contacts are at 2.887 and 2.814 Å

C&E News, 2000, 78, 41

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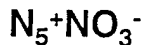
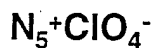
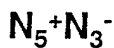
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(In)Compatability of N_5^+



Attempts to couple N_5^+ with energetic anions
can result in explosive reactions !!!



Our goal is the synthesis of an “aromatic” polynitrogen anion with

- A high first ionization potential
- A high activation energy barrier towards decomposition

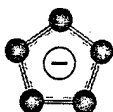
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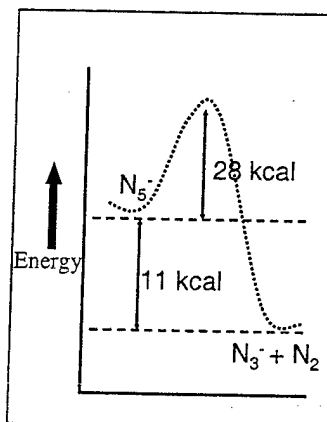


New Polynitrogen Anions as Counterparts for N_5^+



Pentazole anion (N_5^-)

- Theoretical calculations show that this anion has a 28 kcal/mole activation energy barrier for decomposition and its decomposition to N_3^- and N_2 is only 11 kcal/mol exothermic
- Free pentazole has not been isolated to date. Only aryl substituted pentazoles can be isolated and stabilized at low temperatures. These compounds rapidly decompose above 273K to form aryl azides and N_2 gas



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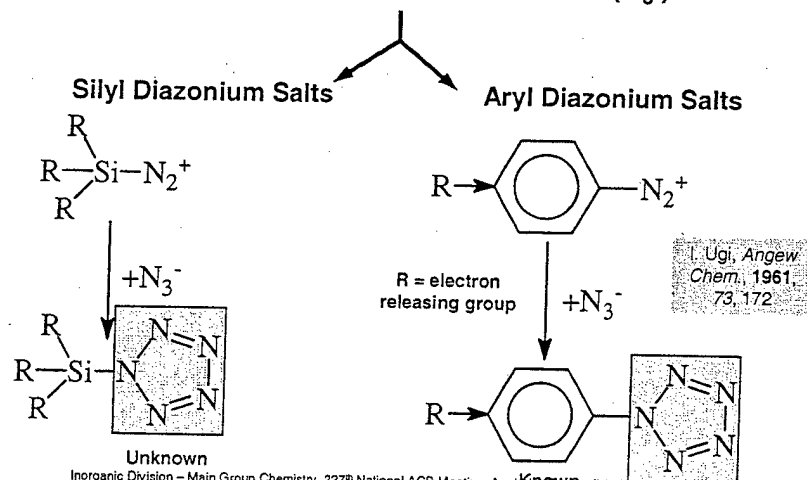


Synthetic Challenge – How do we make These New Anions??



Synthesis of Substituted Pentazoles

Sources for the Pentazole Anion (N_5^-)



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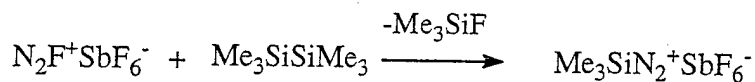
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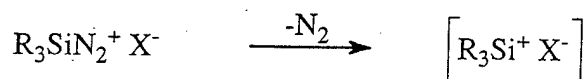
Formation and Stability of Silyl Diazonium Salts



- Failed attempts to synthesize silyl diazonium salts



- R_3SiN_2^+ salts are unstable and spontaneously lose N_2



Theoretical calculations support this experimental observation.

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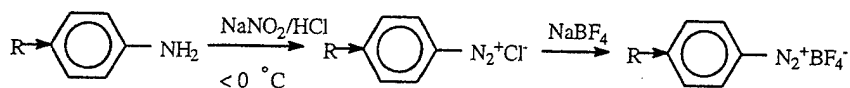
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Synthesis of Aryldiazonium Salts

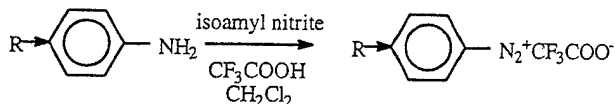


Aqueous Media



Non-aqueous Media

$\text{R} = \text{H, OH, OCH}_3, \text{OC}_6\text{H}_5, \text{OC}_6\text{H}_4\text{N}_2^+, \text{N}(\text{CH}_3)_2$



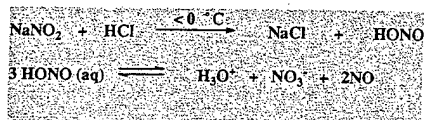
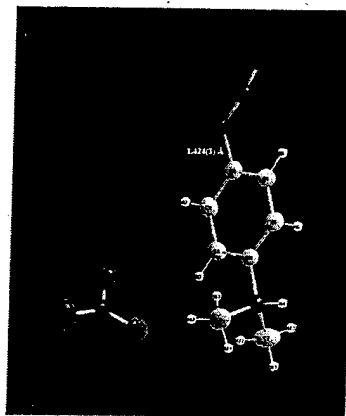
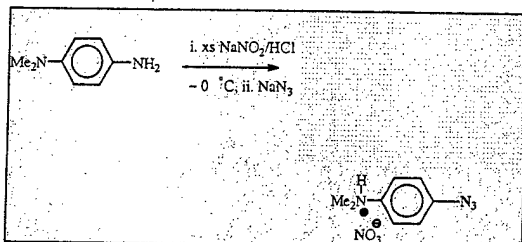
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Pentazole Formation... Not a Trivial Chore !!!



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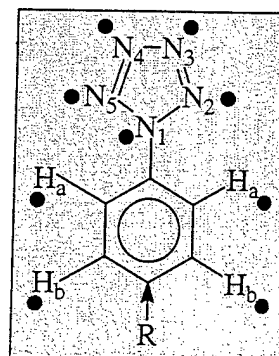


Identification of Arylpentazoles



Pentazoles can be characterized by low temperature NMR spectral studies using ^{15}N labeled samples.

- ^1H NMR: AB-type spectrum with H_a and H_b at 8.0 and 7.0 ppm
- ^{14}N NMR: N_1 at ~ -80 ppm
- ^{15}N NMR: N_2/N_5 at ~ -27 ppm and N_3/N_4 at ~ -4 ppm



Note: Qualitative evidence for the presence of a pentazole ring: N_2 gas evolution in solution

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Cleavage of the Aryl-Pentazole Bond with Retention of the Pentazole Ring



Chemical Methods

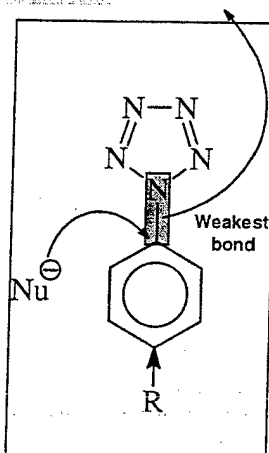
- Ozonolysis does not work! (Ugi, Radziszewski)

V. Benin, P. Kszynski and G. J. Radziszewski, *J. Org. Chem.*, 2002, 67, 1354

- Nucleophilic substitution using strong nucleophiles such as the OH^- , OR^- , F^- etc.

Collisional Fragmentation (ElectroSpray Ion Mass Spectroscopy – ESIMS)

- Electrospray is very gentle and produces high concentration of the parent anion which can be mass selected
- Negative ion detection eliminates interference from neutral or positively charged species



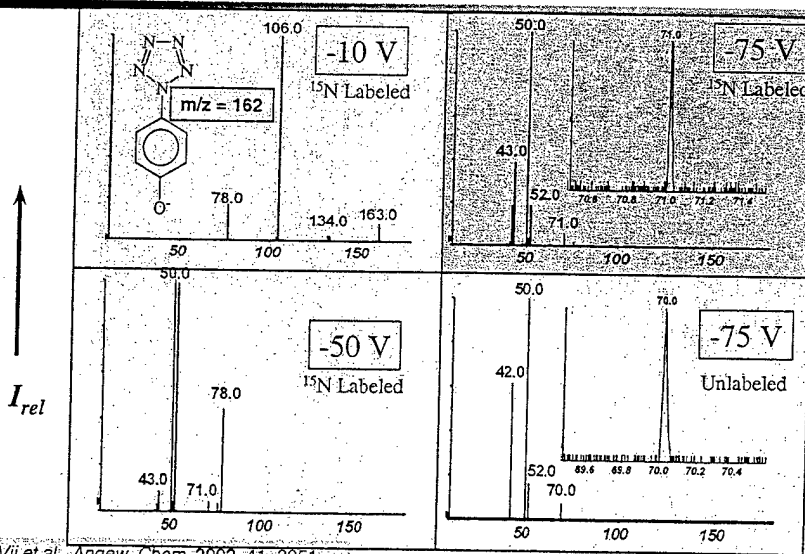
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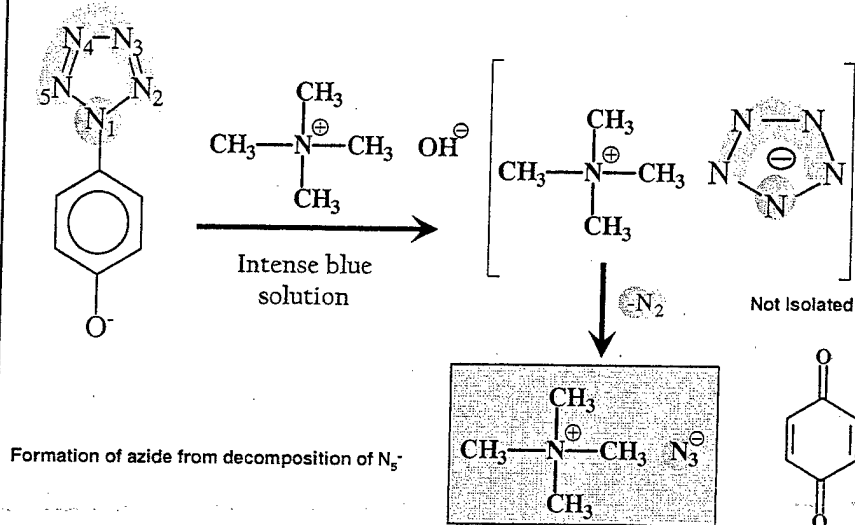


MSMS of the Parent Ion Peak





Chemical Cleavage of the C-N Bond



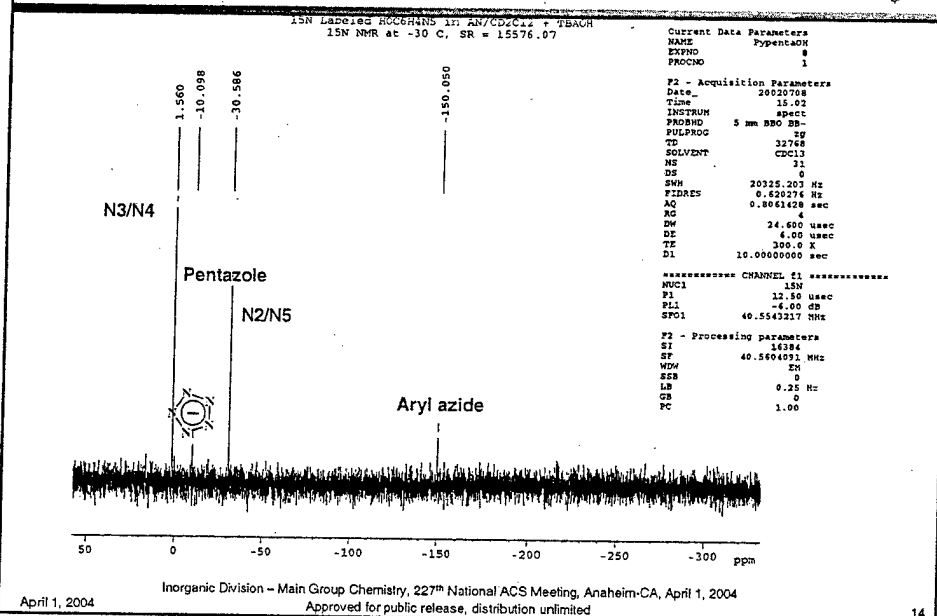
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Aryl-pentazole bond cleavage: N_5^- anion in Solution



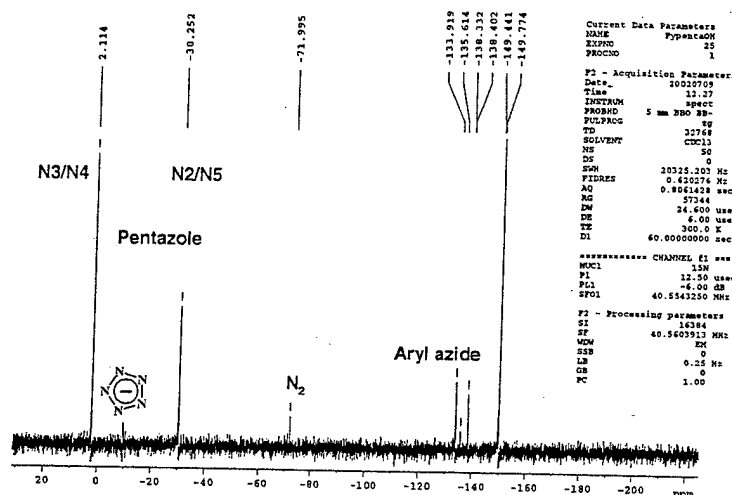
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Subsequent Decomposition of the Pentazole Anion



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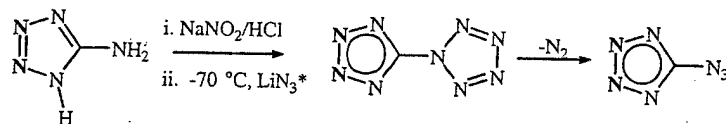
15



Pentazoles with Heterocyclic Substituents



- Tetrazolyl system is unstable above -70 °C and the pentazole ring rapidly decomposes to liberate N₂ gas.



A. Hammerl and T. M. Klapek, *Inorg. Chem.* 2002, 41, 906-912

- In comparison, the pentazole ring derived from 2-amino-4,5-dicyanoimidazole shows higher thermal stability (-30 °C)

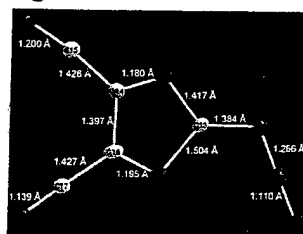
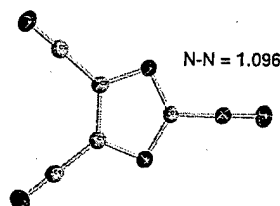
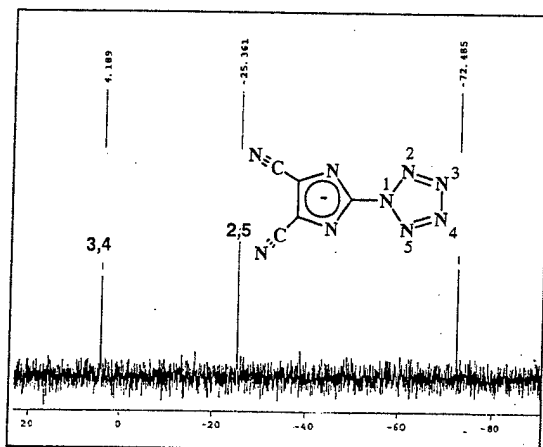
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¹⁵N NMR of 2-pentazoly-4,5-dicyanoimidazole



¹⁵N NMR recorded in a mixture of methanol and acetonitrile at -30 °C, nitromethane used as an external reference (0 ppm)

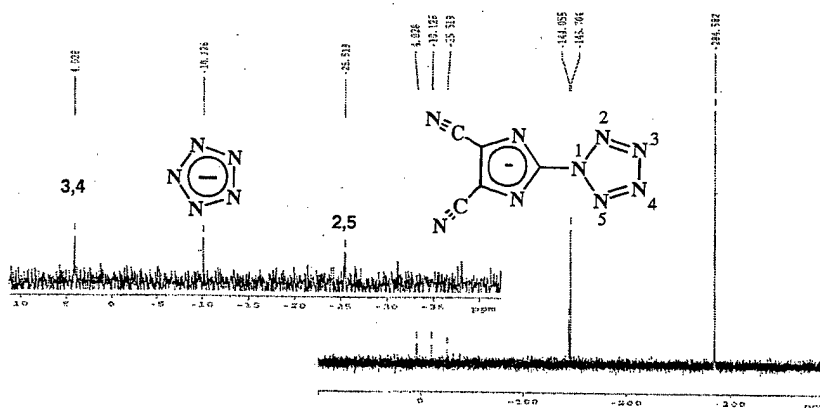
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Pentazolate Anion in Solution ?



- ¹⁵N NMR shows a peak at ~ -10 ppm (-30 °C) upon addition of base, which slowly decomposes to form N₂ and azide ion.
- This peak is also observed upon adding a base to the solution of arylpentazoles at -30 °C.

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18



Chronology of the Pentazolate Anion



- ESIMS of *para*-hydroxyphenylpentazole
Vij, Pavlovich, Wilson, Vij, Christie, Angew. Chem. Intl. Ed. Engl 2002, 41, 3051
Submitted: April 30, 2002; accepted July 3, 2002
- ^{15}N NMR studies showing a peak at -10.2 ppm (-40°C) due to the Pentazole anion resulting from cleavage of *para*-methoxyphenylpentazole which slowly decomposes to form N_2 and azide ion. Upon standing for several days, all peaks disappear!
Butler, Stephens & Burke, Chem. Commun. 2003, 1016
Submitted: February 6, 2003; accepted February 27, 2003
- Laser Desorption Ionization (LDI) time-of-flight (TOF) mass spectrometry of solid *para*- N,N -dimethylaminophenylpentazole shows peaks at m/z : 70 (N_5^-) and -42 (N_3^-). Peak at 70 confirmed by ^{15}N labeling experiment.
Ostmark, Wallin, Brinck, Carlqvist, Claridge, Hedlund & Yudina, Chem. Phys. Lett., 2003, 379, 539
Submitted: Jun. 27, 2003; accepted August 27, 2003

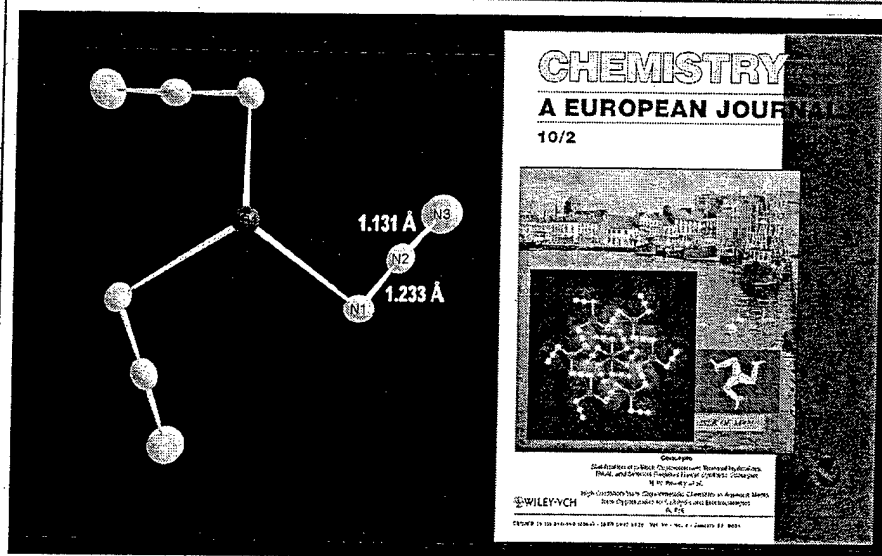
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19



What are “normal” N-N distances in azides?



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20



Abnormalities in azide distances: Artifacts or Structural Contaminants?



- ✓ A large number of crystal structures reported in Cambridge/Inorganic CSD report unusually short $N_{\alpha}-N_{\beta}$ (0.8-1.0 Å) and long $N_{\beta}-N_{\gamma}$ (1.2-1.4) distances.

According to VB theory, in covalently bonded azides,
 $N_{\alpha}-N_{\beta} > N_{\beta}-N_{\gamma}$

Wolfgang, F. and Klapoetke, T. In *Inorganic Chemistry Highlights*; Meyer, G., Naumann, D. and Wesemann, L. Eds.; Wiley-VCH: Weinheim, 2002, Chapter 16 and references therein

- ✓ In most cases, these derivatives were prepared from metal chloride salts and/or recrystallized from chlorinated solvents

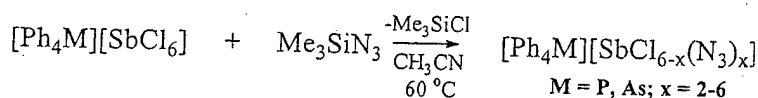
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Reactivity of hexachloroantimonate (VI) with Trimethylsilylazide



- ✓ The substitution of all the six chlorine atoms in SbCl_6^- by the azide groups could not be accomplished in a single step, as reported in literature. The stepwise substitution gives a good insight into the substitution mechanism.

- ✓ Total substitution was achieved after four “refreshment” cycles of the reagents. During the intermediate cycles, the azide content gradually increased from two to five.

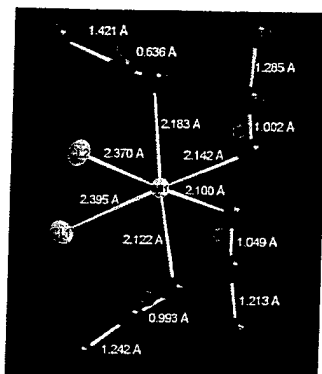
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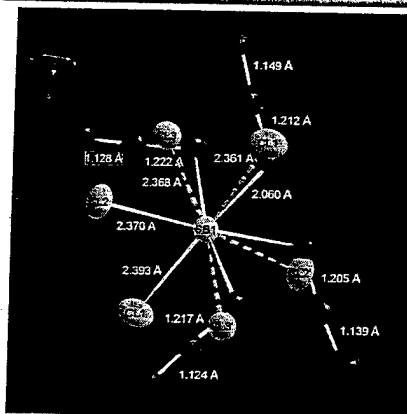
22



The tetraphenylarsonium antimonychloride azide case



Orthorhombic, $P2_12_12_1$
 a, b, c (Å) = 7.7744(14), 13.610(3), 27.094(5)
 $V = 2866.8(10)$, $Z = 4$
 $R = 3.22\%$, $S = 1.088$, highest peak = $0.58 \text{ e}^-/\text{\AA}^3$
Flack's parameter = 0.03(1)



Chloride contamination (%)
NI-N3 = 10; N4-N6 = 18; N7-N9 = 16; NI0-N12 = 37
 $R = 3.22\%$, $S = 1.088$, highest peak = $0.58 \text{ e}^-/\text{\AA}^3$
Flack's parameter = 0.03(1)

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23



Summary



- Synthesized aryl pentazoles: hydroxy group at the *para*-position on the aryl ring gives the best results as observed during this study.
- Demonstrated selective cleavage of C-N bond by ESIMS with retention of pentazole ring. Results confirmed studying ^{15}N labeled pentazoles.
- Experimental detection of pentazolate anion in solution using different substrates.
- Offers potential pathway for bulk synthesis of N_5^- salts
- Chloride ion cause abnormalities in N-N bonds in azides

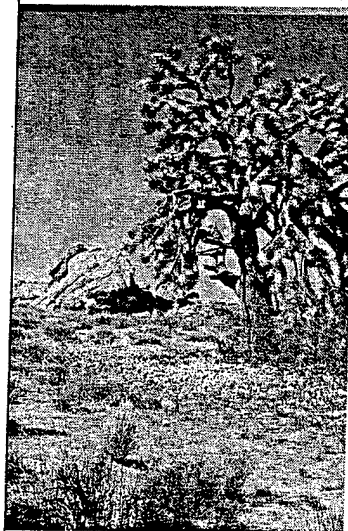
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24



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\$\$\$

Dr. Don Woodbury, Dr. Arthur Morrish (DARPA)

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25



BACKUP

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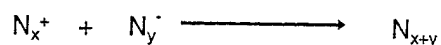
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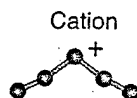
Recipe for Synthesizing Neutral Polynitrogen Compounds



- Combine a polynitrogen cation with a polynitrogen anion to form a neutral polynitrogen compound.

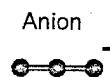


ONLY TWO STABLE POLYNITROGEN IONS KNOWN TO EXIST IN BULK



N_5^+ cation

(discovered in 1999, AFRL, Christie)



N_3^- anion

(discovered in 1890, Curtius)

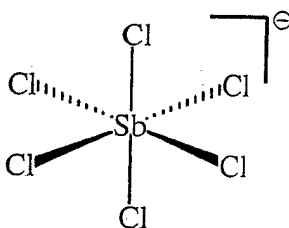
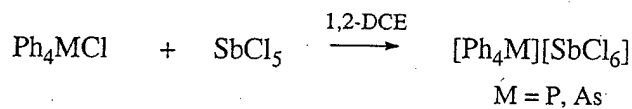
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33



Episode I...Generation of the starting material



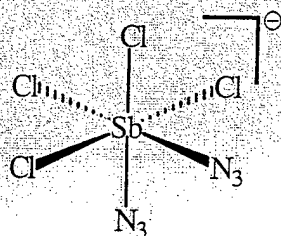
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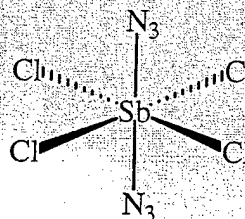
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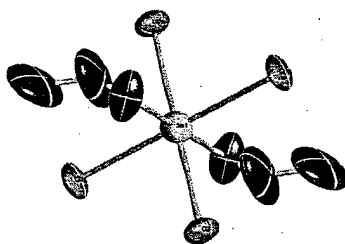
Episode II....cis- or trans- disubstitution with azide groups?



cis-isomer



trans-isomer



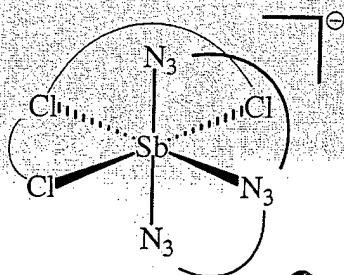
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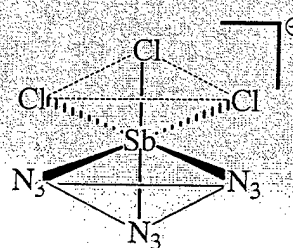
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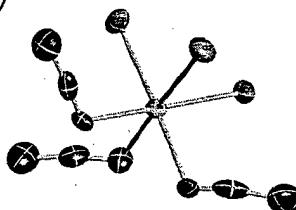
Episode III...Substitution of 3rd chlorine... fac- or mer- isomer ???



mer-SbCl₃(N₃)₃



fac-SbCl₃(N₃)₃



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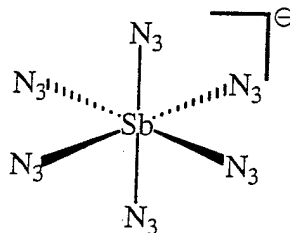
36



Episode VI... Complete substitution of chlorine atoms



No crystal structure obtained yet. However, IR and Raman spectroscopy shows that Sb-Cl bonds are absent i.e., complete substitution by the azide groups.



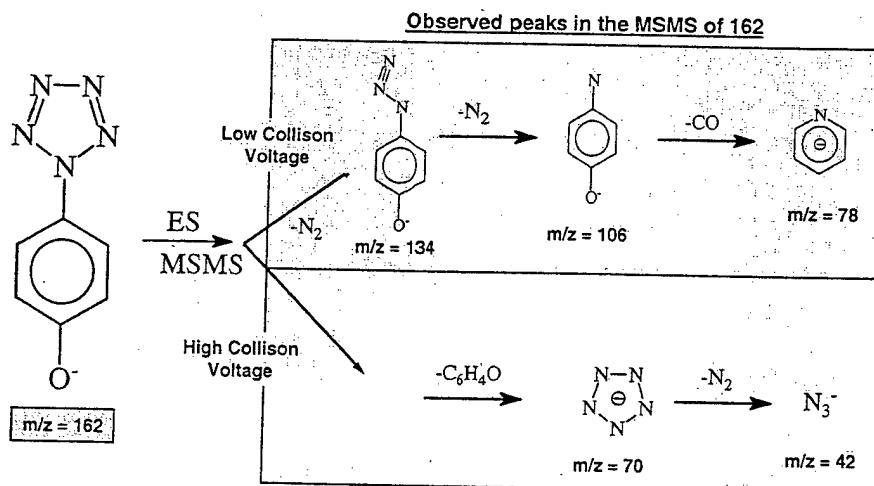
April 1, 2004

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27



ESIMS of para-Phenoxypentazole



Vij, Pavlovich, Wilson, Vj & Christe, *Angew. Chem. Int. Ed.*, 2002, 41, 3051-3054

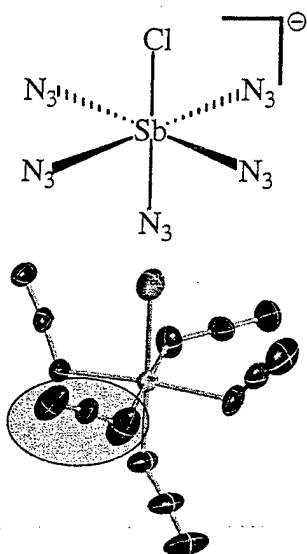
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28



Episode V: Synthesis of Chloropentaazidoantimonate(VI) Anion



The Structure of $\text{Ph}_4\text{PSbCl}(\text{N}_3)_5$

- ✓ The crystals grown from CH_3CN
- ✓ Triclinic space group $P-1$
- ✓ Cell constants: $a = 11.134(3) \text{ \AA}$, $b = 11.663(3) \text{ \AA}$, $c = 13.754(4) \text{ \AA}$; $\alpha = 104.314(5)^\circ$; $\beta = 97.914(5)^\circ$; $\gamma = 115.807(4)^\circ$
- ✓ $Z = 2$
- ✓ $R = 0.0762$
- ✓ All azide distances "normal" except N10-N11-N12

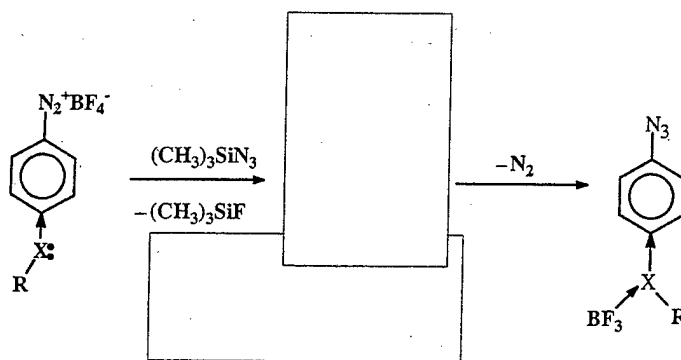
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Reaction with Trimethylsilyl Azide



$\text{X} = \text{N}, \text{O}$

No pentazoles were isolated !!!

Reactions carried out in acetonitrile at -30°C

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38